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Your ref:
Our ref: JDMA/KXS/RMW/P203202WO

BY FACSIMILE

Dear Sirs

Re: **International Patent Application no. PCT/GB03/05565 in the name UNIVERSITY OF NOTTINGHAM et al**

I refer to the Written Opinion dated 3 September 2004 issued in connection with the abovementioned case. The deadline for response is 3 December 2004.

I enclose an amended claim set which is intended to replace the claims currently on file. It is therefore requested that further prosecution of this case proceeds on the basis of the enclosed claim set.

Claims 1 to 11 correspond to previous claims 1 to 11. The applicant has some preliminary results to indicate that the novel methodology disclosed in this patent can be extended to elements from Groups IA, IIA, IIIA, IVA and VA and as such the scope of claim 1 remains unamended. Claims 12 and 13 have been amended so as to be directed towards "anisotropic nanoscale structures". Basis for this amendment can be found on page 3, lines 21 to 23.

Claim 14 has been amended so that the process comprises a sealed heated chamber which comprises a cold finger into which water is placed. Basis for this amendment can be found on page 9, lines 22 and 23.

I also enclose amended pages 3, 3a, 5, 8 and 9.

Page 3 has been amended so as to incorporate a reference to D1 and D2.

Pages 5, 8 and 9 and claim 14 have been amended so that the pressure is defined in metric units and the original definition of the pressure in the units of torr appear in parentheses.

Page 3a, line 5 has been corrected in accordance with Rule 86 EPC so that the term "an isotropic nanoscale structure" is corrected to read "an anisotropic nanoscale structure". Basis for this amendment can be found throughout the specification including page 3, lines 21 to 23. It is clear from the disclosure on page 3, lines 30 and 31 wherein "The present invention aims

to provide a wide range of nanoscale structures such as nanorods, nanofibres and nanotubes" that no other meaning could have been intended.

In Section 1 the Examiner has raised an objection against claims 12 to 15 of the application as being anticipated by the disclosures of D1, D2 and D3.

Claims 12 and 13 have been amended so as to be directed towards an anisotropic nanoscale structure and to the use of an anisotropic nanoscale structure respectively. D1 does not disclose anisotropic nanoscale structures and therefore amended claims 12 and 13 are novel over the disclosures of D1.

D2 discloses a process for the preparation of lithium nitrate by heating lithium in a closed container with nitrogen. Claim 14 has been amended so as to be directed towards a process for producing nanoscale structures from a bulk material, ie nanoscale lithium nitride from bulk lithium nitride. Therefore claim 14 has been amended so as to include a further essential feature of the heated chamber so as to produce the required nanoscale structures wherein the chamber comprises a cold finger into which water is placed.

In Section 2 the Examiner acknowledges that claims directed to lithium nitride with particle size in the nanometer range and with particles which are anisotropic in morphology are both novel and inventive over the disclosures of D1.

In Section 3 the Examiner has raised an objection against the scope of claim 1 as the Examiner has raised an objection against the scope of claim 1 as the Examiner believes that this claim covers an extensive number of compositions. However it is submitted that it would be unduly restrictive on the applicant to restrict claim 1 to lithium nitride only. The application provides a method on page 9 which can be used to produce anisotropic nanoscale structures of claim 1 using at least one element cited from groups IA and IIA of the periodic table and at least one element selected from groups IIIA, IVA and VA. It is submitted that the skilled addressee would not be required to carry out undue experimentation to produce such structures using elements other than lithium and nitrogen. The present application sufficiently discloses a method for enabling the skilled addressee to perform the invention over the entire scope of claim 1 and as such represents a reasonable generalisation of the applicant's findings.

In Section 4 the Examiner has requested that the unit "torr" is replaced by metric units. It is believed that the amendments made to the specification overcomes this objection.

In Section 5 the Examiner has requested that documents D1 and D2 are identified in the description. It is submitted that the amendments made to page 2 of the specification overcomes this objection.

It is submitted that the amendments made to the claims and to the specification overcome the objections raised by the Examiner. Therefore it is requested that the Examiner withdraws the objections raised in the written opinion and issues a favourable IPER.

Kindly acknowledge safe receipt of this letter by returning the enclosed form 1038.

Yours faithfully

Jonathan D M Atkinson
for Urquhart-Dykes & Lord LLP

WO98/24576A discloses "nanostructured" metals, alloys and carbides but these are again approx isotropic nanoparticles of <100 nm diameter.

US5876682 discloses nanostructured nitride ceramic powders of <1000 nm and again these are essentially isotropic materials.

CN1348919A discloses nanosized titanium carbide but again these are nanoparticles and this patent only discloses a single material. Similarly, CN1371863 discloses nanosized titanium boride and again the material is in the form of nanoparticles. This patent also only covers one example.

US5997832 discloses nanorods of metal carbides with diameters <100 nm and aspect ratios of 10-1000 and WO96/30570A discloses nanofibrils of carbides of any metal but in each case there is no disclosure of any nanotube type structure.

US6398125 discloses a process for the preparation of nanosized nitrides comprising heating a molten metal to an ultra-high temperature and atomizing the melt into fine liquid droplets. The stream of droplets is then introduced into a second-stage atomizer chamber and further atomized. The nanometer-sized droplets are then cooled and collected as solid particles.

US42344554 discloses a process for the preparation of lithium nitride by heating lithium in a closed container with nitrogen at a pressure below 100 k pa.

However, the prior art does not disclose any form of nanotube based either entirely or predominantly on material other than carbon or indeed any anisotropic nanostructures based on Group IA metals. The interest in carbon nanotubes arises because of the possibility of allowing step changes in the performance of a wide range of systems. However, the number of applications of carbon nanotubes is limited by the range of structures and electronic properties available. The present invention aims to provide a wide range of nanoscale structures such as nanorods, nanofibres and nanotubes from

materials other than carbon. It is also within the scope of the invention to produce nanoscale structures which incorporate carbon but which would not be classified as carbon nanostructures because of their low (ie less than 50% carbon content).

According to one aspect of the present invention there is provided an anisotropic nanoscale structure formed from at least one element selected from groups IA and IIA of the periodic table and at least one element selected from groups IIIA, IVA, and VA.

In an embodiment, the nanostructure is inorganic.

nanostructure either to produce a non-stoichiometric structure containing lithium, nitrogen and oxygen or to produce a nanostructure effectively based on lithium oxide.

In another aspect of the present invention, there is provided a process for the production of a nanostructure as defined previously, the process comprising exposing the metal of Group IA or IIA to a gaseous source of the element of Group IIIA, IVA, or VA, optionally in the presence of a transition metal, in a sealed heated chamber at a pressure between atmospheric pressure and a pressure of 10^{-2} Pa (10^{-4} torr), wherein the upper limit of the temperature is not more than 1200°C.

Preferably, in the process the upper limit of the temperature is defined by the temperature of decompostion of the compound.

In an embodiment, the process is used to make lithium nitride. In this case, lithium is heated in the presence of nitrogen in a sealed vessel until the pressure in the vessel is constant to form a lithium nitride nanostructure.

Inorganic nanostructures, such as those based on lithium nitride are expected to be of benefit in a number of applications on account of the number of different properties which are available from materials of this type. Thus, for example lithium nitride is a superionic conductor and nanostructures derived from lithium nitride therefore are likely to find application in materials such as rechargeable nano-batteries and other electronic components. This is one application for which carbon nanostructures are clearly unsuitable.

The anisotropic structures of the present invention, including but not limited to rods, fibres, tubes, have a number of applications on account of their properties.

Thus the nanostructures of the present invention have a number of applications such as: ionic conductors/battery components, in hydrogen storage devices, for templating nanowires, electrical devices, catalysis and synthesis, flat screen technology (display

should be at least twice its diameter in order to ensure a favourable temperature gradient. Temperature gradients are particularly important in chemical vapour transport techniques for producing inorganic nanostructures such as those of the chalcogenides.

We have also found that the product only forms if the pressure is reduced below atmospheric pressure. However, we have also found that it is still necessary for there to be a certain amount of gas present in the reactor vessel and it is believed that this behaves as a transport gas. There is, however, a lower limit to the pressure in the reaction vessel and we have found that the synthesis does not progress well below a pressure of 10^{-2} Pa (10^{-4} torr). The upper limit of the acceptable pressure range is atmospheric pressure.

It is also important that the temperature is sufficiently high that the inorganic compound becomes volatile. In the case of lithium nitride a suitable temperature range is between 150°C and 300°C depending on the pressure in the reaction vessel. The upper limit of the temperature is governed by the need to avoid decomposition of the inorganic compound, although some decomposition may be tolerated as it is believed that the individual elements may be transported and recombined in the vapour phase in certain inorganic compounds.

The presence of a transition metal in the reaction vessel during the formation of certain inorganic compounds has been found to be beneficial in producing the nanostructure or to alter the nature of the nanostructure. Thus, in the case of lithium nitride, the presence of iron powder in the reaction vessel leads to an alteration in the manner in which the sheets roll up. Thus, the presence of a transition metal may have a catalytic and/or structure directing effect in the formation of an inorganic nanostructure. In addition, there is the possibility of integrating (substituting) the transition metal into the walls of the inorganic nanostructure.

The present invention will now be illustrated with reference to the example of the preparation of an inorganic nanostructure based on lithium nitride. Lithium nitride can be formed by exposing lithium metal to nitrogen gas at room temperature. Alternatively,

lithium can be heated in the presence of nitrogen. Lithium nitride can also be produced by using molten sodium as a solvent for lithium which is then reacted with nitrogen.

The dissolution of lithium in sodium is carried out in an argon-filled glove box and the sodium is kept molten using a hot plate to provide heating. The molten sodium keeps the argon atmosphere clean by reacting with any residual oxygen gas or water vapour which may be present. The lithium is dissolved in the molten sodium and the crucible containing the mixture is then removed from the hot plate and allowed to cool. Once cool, the crucible is sealed in a reaction vessel in a furnace again in an argon gas atmosphere and heat and nitrogen are supplied. A clump of red fibrous material, consisting of lithium nitride nanotubes, grows above the crucible on a convenient surface provided within the furnace. Suitable surfaces include, for example, a loop of iron wire. The argon gas atmosphere is removed using a suitable pump and is replaced with nitrogen which is introduced under a positive pressure (typically 1.5 atmospheres). The reactants are heated to between 400 and 500°C, preferably about 460°C, for up to 72 hours and the pressure in the reaction vessel is monitored with a pressure transducer to measure pressure changes during the reaction. After a suitable period of time, usually between 6 and 72 hours, the reaction is complete and the point of completion can be measured by the pressure transducer. The pressure in the reaction vessel is constant once the reaction is complete and the vessel is then quenched to room temperature.

The reaction vessel includes a cold finger into which water is then placed and the vessel evacuated to a pressure of 10^{-2} Pa (10^{-4} torr) or less. The vessel is again heated to between 400 and 500°C, preferably about 450°C, for up to 24 hours under a dynamic vacuum in order to distill off the sodium which recondenses on the cold finger. Lithium nitride in the form of a purple crystalline product remains in the crucible and may be collected.

10. A nanoscale structure as claimed in any preceding claim, wherein the nanostructure is a nanotube in which the hollow core has been filled with a metal to form a metallic nanowire.

11. A nanoscale structure as claimed in any preceding claim, wherein chemical modification of the nanostructure has been performed in order to enhance or tailor the properties of the nanostructure.

12. An anisotropic nanoscale structure based on lithium nitride (Li_3N).

13. Use of an anisotropic nanostructure according to any of claims 1 to 12 in an ionic conductor/battery component, a hydrogen storage device, for templating nanowires, an electrical device, catalysis, a flat display screen, or as a structural member.

14. A process for the production of a nanostructure as defined in any of claims 1 to 12, the process comprising exposing the metal of Group IA or IIA to a gaseous source of the element of Group IIIA, IVA, or VA, optionally in the presence of a transition metal, in a sealed heated chamber at a pressure between atmospheric pressure and a pressure of 10^{-2} Pa (10^{-4} torr), wherein the upper limit of the temperature is not more than 1200°C and wherein said chamber comprises a cold finger into which water is placed.

15. A process as claimed in claim 14, wherein the upper limit of the temperature is defined by the temperature of decompostion of the compound.

16. A process as claimed in claim 14 or 15, wherein lithium is heated in the presence of nitrogen in a sealed vessel until the pressure in the vessel is constant to form a lithium nitride nanostructure.

Abstract

The present invention relates to nanotubes and in particular to a process and apparatus for the preparation of nanotubes. In particular, the present invention relates to nanotubes which are made from materials other than carbon or nanotubes containing carbon but which would not ordinarily be classed as carbon nanotubes on account of their low carbon content. The nanostructures of the present invention have a number of applications such as: ionic conductors/battery components, hydrogen storage, templating nanowires, electrical devices, catalysis and synthesis, flat screen technology, and mechanical applications.